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Coupled selective adsorption and ozonation for non biodegradable COD removal

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Abstract

This paper investigates a new water treatment process based on the combined use of the pollutant adsorption onto a mineral surface, and the ozonation of the adsorbed species. Dioxane has been chosen as a model compound as it is refractory towards ozone alone, and two adsorbents (a high silica zeolite FAU and a mesoporous material M) are tested. Three sets of experiments are shown: pollutant adsorption alone, pollutant ozonation alone and the coupled adsorption/ozonation process. The first results show that FAU is not a well suited adsorbent, as dioxane adsorption itself is weak and, moreover, the coupled process does not induce any benefit. On the other hand, mesoporous material M gives better results, since dioxane removal has been achieved up to 50%. The difference between the two materials is attributed to their catalytic effect: whereas FAU does not react with ozone, M probably decomposes the oxidant, generating free radical species and thus acting as an advanced oxidation process.

Introduction

In a next future, environmental standards and regulations will still become more restricting as regards the quality of water and wastewater. Beyond usual processes, it will be often necessary to use additional treatments such as chemical oxidation (ozonation or AOPs) or adsorption. These processes show limits in terms of cost and of handling: slow kinetics for low concentration compounds, competition towards ozone consumption or adsorption in the case of brines, selectivity and regeneration of adsorbents. So, the design of economically viable processes will require to improve the kinetics and, specifically, will require to aim ozone or adsorbent action towards the undesirable compound.

In that context, recent studies have investigated the interaction between ozone and a solid phase either for ozone and/or pollutant concentration on the adsorbent surface [1], or towards ozone catalytic decomposition into less selective radical species, in order to enhance reactivity towards the pollutant [2]. Zeolites, TiO_2 , supported metals or modified activated carbons are most commonly used.

Relying on a process developed at INSA Toulouse for COV abatement through coupling zeolite adsorption and ozonation [3], the present study intends to apply a similar process to liquid effluents. It reports preliminary tests regarding dioxane removal, either by ozone alone, by adsorption itself and by coupling the two processes. Two adsorbents are tested: an hydrophobic zeolite: dealuminized Faujasite Y (FAU), and an amorphous mesoporous material (M). The effect of ozone on the adsorbent is also reported.

Materials and methods

Adsorbents: The two adsorbents are first chosen for their hydrophobicity, in order to avoid adsorption competition between the solvent (water) and the solutes (dioxane and/or ozone). Hence two molecular meshes are tested, differing from their composition (aluminosilicate or silicate), their pore size and their crystalline structure. The main characteristics of these adsorbents are shown in Table 1.

Table 1: Adsorbents main characteristics

Adsorbent	Dealuminized Faujasite Y (FAU)	Mesoporous material (M)
Particles size (μm)	6 - 8	2 – 3
Structure	Crystalline	Amorphous
Pore diameter (\AA)	13	22
Si/Al ratio	200	Silicate only

Ozone/adsorbent interaction: Ozone is produced from an air/ O_3 generator and bubbled in a suspension of adsorbent in 250 mL pure water at room temperature (20°C). After 12 h, the solution is filtered, the solid is dried (150°C during 24 h) and analysed for BET specific area and X ray diffraction.

Dioxane adsorption isotherms and kinetics are determined by volumetric methods. An aliquot of adsorbent, weight m , is introduced into a solution of pollutant, initial concentration C_0 , volume V (1.5 L), under agitation (10 rpm) at room temperature. Periodically, 10 mL samples are collected and filtered ($0.45 \mu\text{m}$) and the remaining dioxane is measured by gas chromatography. A mass balance gives the adsorbed quantity q_t according to Equation 1. Time (t) evolution of this parameter gives the adsorption kinetics and at the final steady state, the equilibrium adsorption capacity q_e is obtained.

Ozonation and adsorption/ozonation coupled experiments are carried out in a semi-batch bubble column reactor (15 cm inner diameter) filled with 8.5 L solution. The temperature is controlled to 20°C using an immersed heat exchanger and the pH is controlled to 3. Ozone is produced from a O_2/O_3 generator (Trailgaz) and bubbled at the bottom of the reactor. At the inlet and outlet, O_3 concentrations in the gas are measured using a UV analyser (Ozomat GM-6000-OEM). In the liquid, O_3 is analysed by a polarographic probe (Orbisphere Laboratories). Liquid samples (10 mL) are periodically collected for analysis. Figure 1 shows a schematic representation of the experimental setup used in this part of the study.

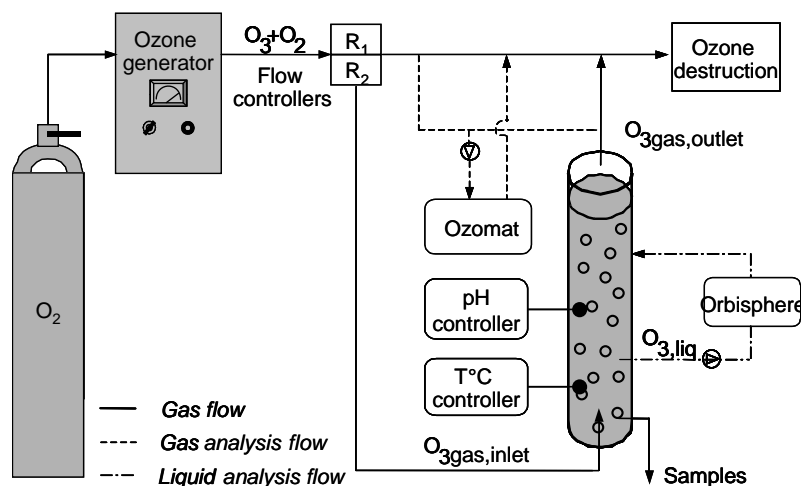


Figure 1: Schematic diagram of the experimental setup

Results and discussion

Ozone/adsorbent interaction: 24 h contact between ozone and the adsorbents does not modify the solid structures. Indeed, the X Ray diffractograms (shown in Figure 2) before and after contact are totally identical. It is noticeable that the diagrams show a great difference between the two adsorbents due to the crystal structure: Faujasite is a crystalline compound, which explains the different peaks in the diffractogram, whereas M is an amorphous one, so that no diffraction peaks are detected.

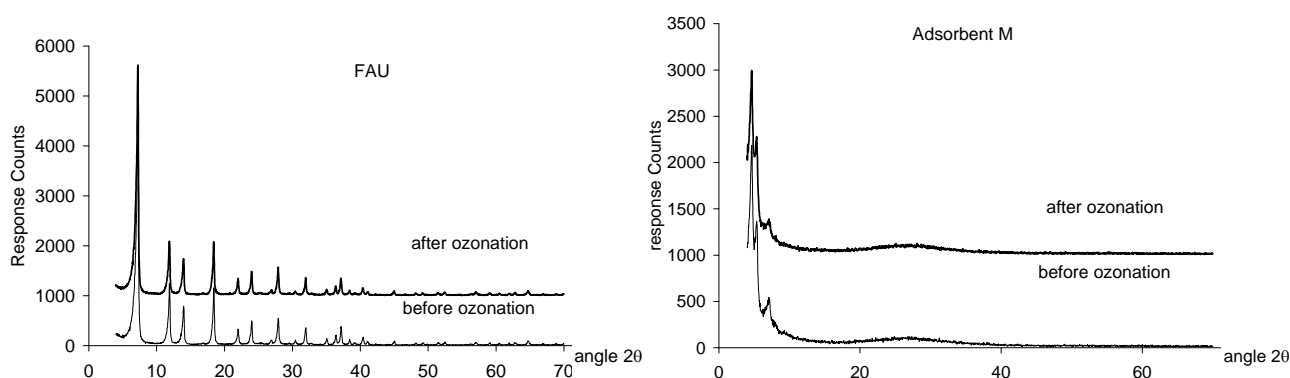


Figure 2: Adsorbents X-ray diffractograms before and after ozonation

On the other hand, an increase of specific surface is observed, as shown in Table 2. It can be attributed to a surface “cleaning” by the oxidant. Indeed, organic matter, like surfactants remaining from the solid synthesis process, could be adsorbed onto the solid surface, and thus be removed after surface reaction with ozone.

Table 2: Adsorbents BET specific area (m²/g)

Adsorbent	Before ozonation	After ozonation	Variation
FAU Y	450	560	+ 25%
M	610	860	+ 40%

Table 3: Dioxane / FAU kinetic parameters

Parameter	Value
q _e (mg _{dioxane} /g _{FAU})	11.66
k (g _{FAU} /mg _{dioxane} /h)	0.76
Reg. coeff. R ²	0.998

Dioxane adsorption. The adsorption isotherms have been determined after 12 h contact in agitated 250 mL solutions. Either the adsorbent mass was fixed and the pollutant concentration was varied, or the other way round (fixed C₀ and varying m). A discrepancy in the results (not shown) has been observed depending on the experimental conditions, yet it can be concluded that in all cases, dioxane adsorption onto FAU is not favoured.

Moreover Figure 3 plots the time evolution of dioxane concentration in the presence of FAU. As can be seen, a plateau is reached after 80 min contact, the adsorption capacity remains quite low. These kinetics follow a second order law [4], as shown by Equation 2 and Table 3.

Equation [1]

$$m \times q_t = V(C_{t=0} - C_t)$$

Equation [2]

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

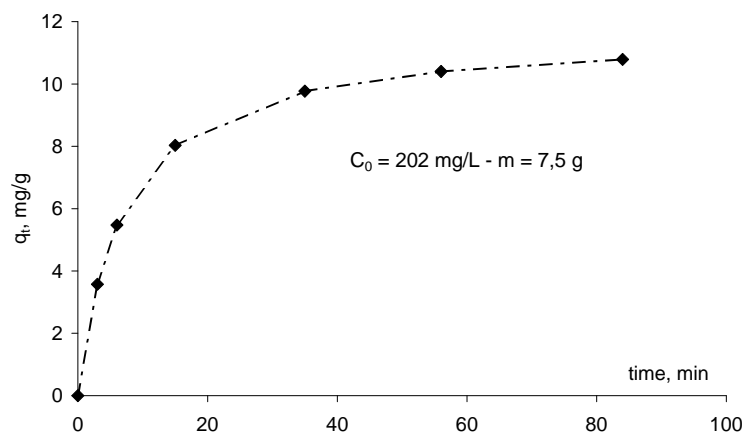


Figure 3: Adsorption kinetics onto FAU

Ozone/dioxane/adsorbent interaction: Figure 4 and Figure 5 illustrate the tests carried out. They show the time evolution of the O₃ concentration in the gas phase at the reactor outlet, the O₃ concentration in the liquid and the dioxane concentration in the liquid, for the two adsorbents. In both cases reference experiments are plotted, i.e. ozone dissolution in pure water and dioxane ozonation without adsorbent.

First, it is evidenced that ozone alone does not oxidize dioxane as the concentration profiles are similar; the difference is only due to small changes in the O₃ inlet concentration. Secondly, the coupled process with FAU leads to a slight decrease of dioxane in the liquid (Figure 4). Thus this pollutant concentration decrease is only due to adsorption onto FAU, as shown in Figure 6 where the relative dioxane decrease in the liquid phase is reported for both experiments (i.e. adsorption alone as in Figure 3 and coupled process as in Figure 4).

On the other hand, mesoporous material M gives better results: In experiments of ozone adsorption onto M, O₃ concentration in the liquid remains zero, which indicates its adsorption and decomposition onto M. Further experiments have to be carried out, particularly in the long term, to elucidate this mechanism. Moreover, in the coupled dioxane adsorption/ozonation test, a technical problem did not allow monitoring of the O₃ concentration in the liquid phase. It is also likely that this parameter value also remains zero, all the more than a part of the ozone supplied is used towards

dioxane oxidation. Yet, ozone decomposition into radical species seems to be the more likely hypothesis. Büchel *et al.* [5] have already reported such a radical mechanism during mesoporous materials regeneration by gaseous ozone, in the presence of moisture.

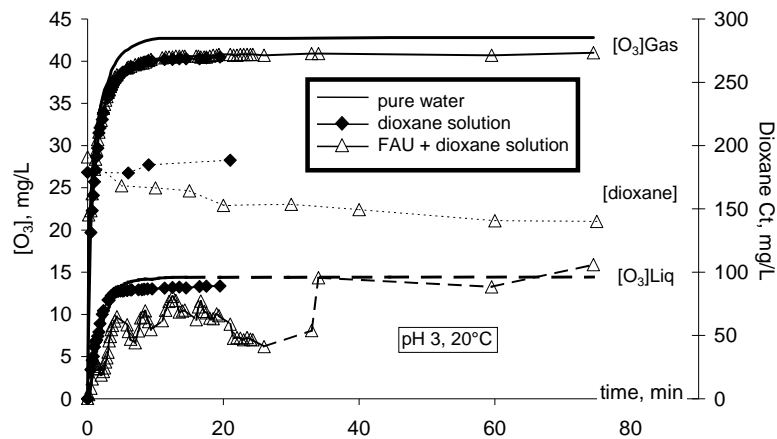


Figure 4: Ozonation tests of dioxane onto FAU

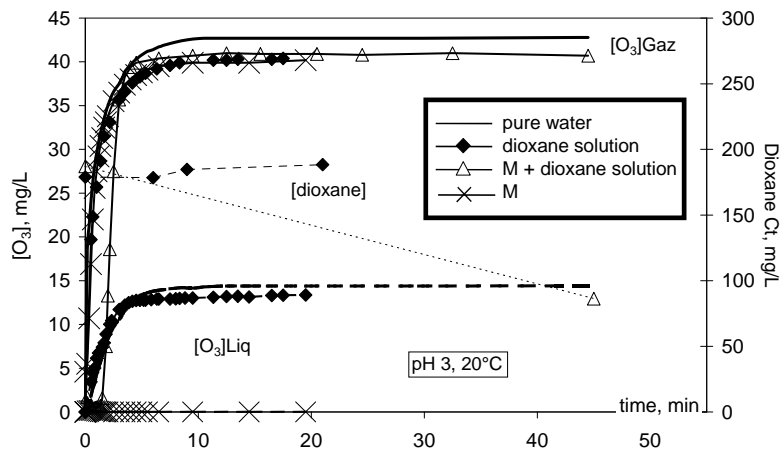


Figure 5: Ozonation tests of dioxane onto M

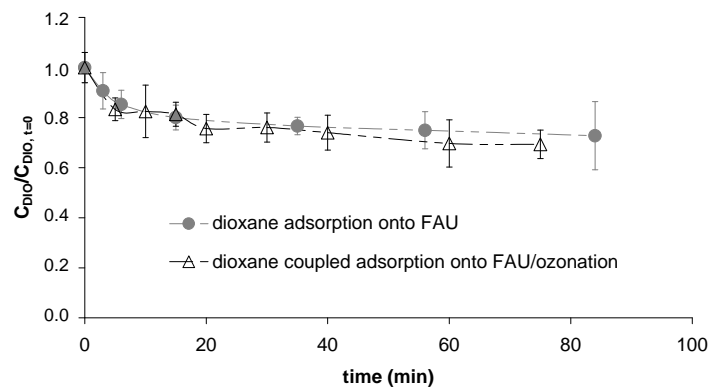


Figure 6: Dioxane compared adsorption and coupled adsorption/ozonation onto FAU

Moreover, dioxane concentration is reduced to 50% after 45 min coupled treatment (Figure 5). This also points out a noticeable catalytic activity of this adsorbent. Nevertheless, additional single adsorption experiments of dioxane onto this adsorbent have to be carried out in order to confirm the catalytic effect observed in the presence of ozone.

Conclusions

This preliminary study evidences the benefits of coupling oxidation and adsorption processes for recalcitrant COD removal. It also points out the crucial issue of the adsorbent choice. Several points are to be settled and additional experiments are under way, in particular screening of both the potential adsorbents and the target molecules. New methods are developed in order to understand the role of each step and the mechanism that governs the process. At last, a new pilot scale reactor is to be developed to test industrial feasibility under the different possible configurations.

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